

ON THE INTERNAL PRESSURE OF STRONG ELECTROLYTES

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ABSTRACT

It is shown that the difference in thermal properties of dilute solutions against those of the pure solvent is due to the superposition of two effects: 1. A physical effect of the ion on the solvent which is manifested as an internal pressure varying from point to point in the solution. This pressure distribution is calculated for aqueous solutions of monovalent salts by an approximation theory in which the effect of the so-called ion atmosphere is estimated by means of the Debye-Hückel potential. In this, as in ensuing calculations, the thermal properties of the solvent are assumed to be known. The effect of this internal pressure on the thermal coefficient of expansion and on the compressibility of dilute binary solutions is calculated and the results are found to be in satisfactory agreement with experimental values. 2. Definite evidence is obtained that the second effect determining the thermal properties of solutions is due to a chemical action of the ion on the solvent. This effect increases linearly with the molal concentration. As a result of the present paper and previous work, to which reference is given, we can say that the caloric as well as the thermal behaviour of dilute solutions is duly accounted for.

I. COMPUTATION OF THE INTERNAL PRESSURE

IN A previous paper¹ the pressure distribution in a strong electrolyte of moderate concentration was calculated in connection with a detailed analysis of the specific heat of solutions. It is the purpose of the present paper to improve somewhat on this calculation, in that account will be taken of the so-called ion atmosphere.² As applications we shall consider the effect of this pressure distribution on the compressibility and on the thermal coefficient of expansion of aqueous solutions of monovalent salts.

As in the paper¹ already referred to, we shall choose as our starting point for the calculation of pressure the general expression for ponderomotive force on a dielectric, derived by Dällenbach;³

$$k_i = \rho E_i + P_k \frac{\partial E_i}{\partial x_k} + \frac{4}{5} \pi \left\{ \frac{\partial P_k}{\partial x_k} P_i + \frac{\partial P_i}{\partial x_k} P_k + \frac{\partial P_k}{\partial x_i} P_k \right\} \quad (1)$$

where k_i is the i -component of force density, (force per unit volume), ρ is the true charge density, E_i is the i -component of electric field, and P_i is the i -component of electric polarization. The expression is to be summed over double indices.

¹ F. Zwicky, *Phys. Zeits.* **26**, 664 (1925); **27**, 271 (1926). F. Zwicky, *Proc. Nat. Acad.* **12**, 86 (1926).

² S. R. Milner, *Phil. Mag.* **23**, 551 (1912). Debye and Hückel, *Phys. Zeits.* **24**, 185 (1923).

³ W. Dällenbach, *Phys. Zeits.* **27**, 632 (1926). It is doubtful whether the term ρE_i should be left in the expression, as the ions undoubtedly are somewhat accelerated by the field, and thus do not contribute by the full amount ρE_i to k_i . We have shown, however, that leaving out this term makes a difference of only about 1 percent in the computed pressures for aqueous solutions.

For the derivation of Eq. (1) the assumption has to be made that, in the region considered, our medium is isotropic. The formula also holds for a crystal of the regular system. Otherwise the expression is perfectly general, and not restricted to any special functional relation between electric polarization and electric field. For small electric fields the polarization is proportional to it. For strong electric fields the polarization becomes more and more independent of the field strength due to saturation of the dielectric. Consequently the dependency of P on E in our field will vary with the radial distance from the ion. It has been shown before¹ that a very good approximation is obtained by considering two regions, one outside a certain critical radius, r_k , and one inside. In the first region the polarization is calculated by means of the ordinary dielectric constant, whereas in the second region we use its saturation value. The latter is essentially obtained by multiplying the dipole moment by the number of molecules per cc. The critical radius, r_k , will be defined as the value of r for which the polarization as computed by the two methods is the same.

Region 1 ($r > r_k$). Let the field be some function $E(r)$ of r which will be specified later. Then:

$$P = (D - 1)E(r)/4\pi \quad (2)$$

where D is the dielectric constant.

Referring to rectangular coordinates, we can establish the following relations for the components:

$$E = E_k x_k / r; \quad E_i = E x_i / r; \quad P = P_k x_k / r$$

$$\frac{\partial E_i}{\partial x_k} = \frac{\partial E_k}{\partial x_i} = \frac{x_i x_k}{r^2} \frac{dE}{dr} + \frac{E}{r} \left\{ -\frac{x_i x_k}{r^2} + \delta_{ik} \right\}; \quad \delta_{ik} = \begin{cases} 1, & i = k \\ 0, & i \neq k \end{cases}$$

Substituting these quantities into (1) one obtains after some easy transformations:

$$|k| = |E| \left\{ |\rho| + \frac{D-1}{4\pi} \left| \frac{dE}{dr} \right| + \frac{4\pi}{5} \left(\frac{D-1}{4\pi} \right)^2 \left[|\operatorname{div} E| + 2 \left| \frac{dE}{dr} \right| \right] \right\}.$$

And since, $\operatorname{div} (D \cdot E) = 4\pi\rho$; $\operatorname{div} E = 4\pi\rho/D$

We get:

$$|k| = |E| \left\{ |\rho| \left(1 + \frac{(D-1)^2}{5D} \right) + \frac{D-1}{20\pi} \left| \frac{dE}{dr} \right| (3 + 2D) \right\} \quad (3)$$

The absolute values can be used as shown because ρ and dE/dr always have the same sign.

For the potential of the field we shall use the value derived by Debye and Hückel:⁴

$$\psi = \frac{\nu e}{D} \frac{e^{-kr}}{r}$$

⁴ Reference 3. This will give us an estimate of the influence of the space charge effect on the pressure, at least for small concentrations.

And consequently,

$$\left. \begin{aligned} \rho &= -\frac{D}{4\pi} \nabla^2 \psi = -\frac{D}{4\pi} \kappa^2 \psi \\ E &= -\frac{\partial \psi}{\partial r} = \psi \left\{ \kappa + \frac{1}{r} \right\} \\ \frac{dE}{dr} &= -\psi \left\{ \kappa^2 + \frac{2\kappa}{r} + \frac{2}{r^2} \right\} \end{aligned} \right\} \quad (4)$$

In these expressions ϵ is the elementary charge $= 4.77 \times 10^{-10}$ e.s.u. and ν is the valency of the ion.

$$\kappa = [8\pi n(\nu\epsilon)^2 / DkT]^{1/2}$$

where $k = 1.37 \times 10^{-16}$ ergs, (Boltzmann's constant), and n = the number of ions per cc.

Substituting the values (4) into (3), one gets after some transformations:

$$|k| = \frac{\psi^2}{20\pi} \left\{ \alpha\kappa^3 + (\alpha + 2\beta) \frac{\kappa^2}{r} + 4\beta \frac{\kappa}{r^2} + \frac{2\beta}{r^3} \right\} \quad (5)$$

where

$$\alpha = 3D^2 + 4D - 2 \quad \text{and} \quad \beta = 2D^2 + D - 3.$$

The pressure is obtained by integrating k over r :

$$p = \int_r^\infty |k| dr = \frac{\beta(\nu\epsilon)^2}{40\pi D^2} \frac{e^{-2\kappa r}}{r^4} \left\{ \frac{\alpha}{\beta} \kappa^2 r^2 + 2\kappa r + 1 \right\} \quad (6)$$

Region 2 ($r < r_k$). The second region turns out to be comparatively small, and it is easily seen that here one may safely neglect the effect of the space charge. The error introduced in the pressure by so doing is not more than a few percent. In applications there is a more serious source of error in this region due to the uncertainty about the thermal properties of the solvent at the extremely high pressures in the neighborhood of the ion. These sources of error, however, are offset by the smallness of the region, i.e. in integrating for the thermal properties of the solution as a whole, the contribution from the region of uncertainty is small.

We shall therefore neglect the effect of space charge in this region, and write:

$$P = N\mu; \quad \frac{dP}{dr} = 0; \quad E = \frac{\nu\epsilon}{r^2} - 4\pi N\mu$$

so that,

$$|k'| = N\mu \left[2 \frac{\nu\epsilon}{r^3} - \frac{8\pi}{5} \frac{N\mu}{r} \right]$$

where N is the number of molecules per cc of solvent.

If by p_k we denote the value of the pressure at the critical radius, then,

$$\left. \begin{aligned} p &= p_k + \int_r^{r_k} |k'| dr = p_k + \Delta p \\ \Delta p &= N\mu\nu\epsilon \left\{ \frac{1}{r^2} - \frac{1}{r_k^2} \right\} - \frac{8\pi}{5} N^2 \mu^2 \ln \frac{r_k}{r} \end{aligned} \right\} \quad (7)$$

where

As we have already mentioned, the value of the critical radius is given by:

$$\frac{D-1}{4\pi} E(r_k) = \frac{D-1}{4\pi} \frac{\nu\epsilon}{D} \frac{e^{-\kappa r_k}}{r_k} \left\{ \kappa + \frac{1}{r_k} \right\} = N\mu.$$

Expanding and neglecting terms of the order $(\kappa r_k)^3$ and higher, this gives:

$$r_k = \left(\frac{4\pi N\mu}{\nu\epsilon} + \frac{\kappa^2}{2} \right)^{-1/2}. \quad (8)$$

In order to carry through the numerical computations we must make an assumption as to the value of μ . The dipole moment of a single water molecule can be deduced from measurements of the dielectric constant of water vapor. In this way one finds $\mu_1 = 1.8 \times 10^{-18}$ e.s.u. This value, however, cannot be used on account of polymerization. In the paper¹ already referred to, it was shown by a very general consideration that the average value of μ in water must be less than 9×10^{-19} e.s.u. It is found that the best quantitative agreement with experimental results is obtained by adjusting μ to about 5×10^{-19} e.s.u. With this value we find for aqueous solutions of monovalent salts the pressure distribution given in Table I. Γ stands for concentration in mols per 1000 grams of solvent.

These values must be further modified because our theory, while it takes account of the space charge, paradoxically so to speak, neglects the presence of the individual ions making up that space charge. It is clear that at some point in between a positive and negative ion the pressure effect must be zero, while by our theory it extends to infinity. In other words, the integration (6) should have been carried out to some finite upper limit rather than to infinity. As a somewhat arbitrary correction which, however, cannot be very far off, we propose the following: Depress the whole pressure scale by an amount equal to the pressure, p_0 , at a distance r_0 from the ion, and let this distance be given by the relation:

$$(4\pi/3)r_0^3\Gamma 2n_0 = V \quad (9)$$

where V is the volume of a solution containing 1000 gr solvent, and n_0 is the Loschmidt number $= 6.06 \times 10^{23}$.

Table II gives the pressure distributions corrected as here stated. With increasing concentrations the reliability of the figures decreases. Aside from the various approximations made in this development, there are es-

entially two sources of error. In the first place, no account is taken of the chemical action of the ion on the solvent, an effect which so far does not permit of quantitative treatment. In the second place the effect of the ion atmosphere at high concentrations is not rigorously given by the Debye-Hückel potential. For a rigorous treatment of this effect statistical methods would have to be used⁵. The mathematical difficulties of such a theory, however, so far have been insurmountable.

As another, probably small, source of error, it should be mentioned that this theory does not take account of any pressure dependence of the dielectric constant. It has been shown by Roentgen,⁶ Falckenberg,⁷ and others that the pressure dependence of the dielectric constant of water is very small up to 200 kg/cm.² No experimental data are available for pressures higher than this.

TABLE I. Pressures in kg/cm.². Water at 20°C.

Γ	$r=1A$	2	3	4	5	6	7	8	9	10
0.1	76000	16000	5229	1702	522	237	117	66	38	23
0.15	76000	16000	5020	1579	474	217	106	56	32	18
0.3	75000	15330	4628	1214	406	169	78	38	—	—
0.5	74800	15036	4288	980	294	124	52	—	—	—
1.0	74580	13880	3205	687	199	—	—	—	—	—
2.0	72350	12170	2000	380	—	—	—	—	—	—

TABLE II. Pressures in kg/cm.² Water at 20°C.

Γ	r_0	$r=1A$	2	3	4	5	6	7	8	9	10
0.1	12.5A	76000	16000	5220	1695	515	230	110	57	29	14
0.15	10.9	76000	16000	5010	1568	463	206	95	45	20	7
0.3	8.66	75000	15300	4604	1190	382	145	54	14	—	—
0.5	7.3	74800	14977	4247	940	253	83	11	—	—	—
1.0	5.8	74500	13800	3124	606	118	—	—	—	—	—
2.0	4.6	72200	12020	1850	227	—	—	—	—	—	—

2. APPLICATIONS

(a). *The thermal coefficient of expansion.* When a solution is heated from T to $T+\Delta T$ at constant external pressure, the internal parts of the liquid expand at variable pressures. If we consider a spherical shell of radius r and thickness dr around the ion, the expansion per degree rise in temperature will be: $d(\Delta V)/dT = dn dv/dT$ if $dn = 4\pi r^2 dr/v$ be the number of mols in the spherical shell.

Total expansion:

$$\frac{dV}{dT} = n \int_0^{r_0} \frac{1}{v} \frac{dv}{dT} 4\pi r^2 dr$$

⁵ S. R. Milner, Phil. Mag. **23**, 551 (1912).

⁶ W. C. Roentgen, Wied. Ann. **52**, 593 (1894).

⁷ G. Falckenberg, Ann. d. Physik **72**, 191 (1923).

and

$$\alpha_s = \frac{1}{V} \frac{dV}{dT} = \frac{3}{r_0^3} \int_0^{r_0} \frac{1}{v} \frac{dv}{dT} r^2 dr.$$

Now,

$$\frac{dv}{dT} = \left(\frac{\partial v}{\partial T} \right)_p + \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{dp(r)}{dT} \right)_r.$$

So that,

$$\alpha_s = \frac{3}{r_0^3} \int_0^{r_0} \left\{ \alpha(r) - \kappa(r) \left(\frac{dp(r)}{dT} \right)_r \right\} r^2 dr$$

where $\alpha(r)$ is the thermal coefficient of expansion at the pressure $p(r)$, and $\kappa(r)$ is the compressibility at this pressure, or

$$\alpha_s - \alpha_0 = \frac{3}{r_0^3} \int_0^{r_0} \left\{ \alpha(r) - \alpha_0 - \kappa(r) \left(\frac{dp(r)}{dT} \right)_r \right\} r^2 dr \quad (10)$$

where α_0 is the coefficient of expansion of the pure solvent under the given conditions of external pressure and temperature. It turns out that the isothermal expansion represented by the third member of the integrand is quite small compared with the isobar expansion $\alpha(r)$. This isothermal expansion therefore may be neglected in first approximation. The quantity (10) is to be calculated from graphical integration. The variation in thermal coefficient of expansion for pure water for pressures varying from 0 to 8000

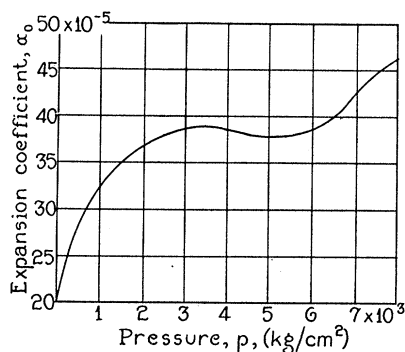


Fig. 1. Coefficient of thermal expansion α_0 of water at 20°C.

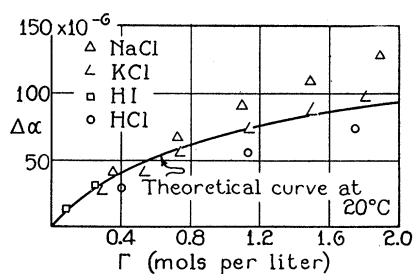


Fig. 2. $\Delta\alpha$ for solutions of NaCl, KCl, HI, HCl at average temperature of 22.5°C as function of concentration.

kg/cm² are given by Bridgman⁸ and reproduced in Fig. 1. Beyond this upper pressure one must be satisfied by rather dubious extrapolations, but these high pressures occur only in very small regions of the solution, and contribute little to the total effect.

⁸ Bridgman, Proc. Am. Ac. Arts and Sciences, **48**, 309 (1912-13); Bridgman, Critical Tables, **III**, 40 (1928).

The pressure effect, calculated, as here outlined, is shown graphically as a function of concentration in Fig. 2. The experimental values are taken from the critical tables.⁹ The good agreement exhibited may be accidental to some extent but certainly not altogether. There is a definite qualitative agreement, and that is all we can expect, since, (by necessity), no account is taken of hydration effects in the present treatise. The experimental values for the thermal coefficient of expansion do not permit of a closer analysis of the hydration effect. In the case of the compressibility of solutions, however, we shall see definite evidence of the part played by chemical action of the ion on the solvent in determining the thermal properties of solutions.

(b). *Compressibility.* When the external pressure, p_0 is changed from p_0 to $p_0 + \Delta p_0$ the pressure in the interior is changed by say an amount Δp which we must determine. Consider again a spherical shell of radius r and thickness dr , containing dn mols of water. When the external pressure is increased, the change in volume of this shell will be:

$$d(\Delta V) = dn \Delta v = \frac{1}{v} \Delta v 4\pi r^2 dr.$$

Total change:

$$\Delta V = \int_0^{r_0} \frac{\Delta v}{v} 4\pi r^2 dr.$$

Consequently:

$$\kappa_s = -\frac{1}{V} \frac{\Delta V}{\Delta p_0} = \frac{3}{r_0^3} \int_0^{r_0} \left\{ -\frac{1}{v} \frac{\Delta v}{\Delta p_0} \right\} r^2 dr.$$

Now, as the external pressure is increased, the radius of the shell under consideration is decreased, thereby making the internal pressure change by an amount:

$$\Delta p = \Delta p_0 + \frac{\partial p(r)}{\partial r} \Delta r.$$

Hence

$$\frac{\Delta p}{\Delta p_0} = 1 + \frac{\partial p(r)}{\partial r} \frac{\Delta r}{\Delta p_0}.$$

And

$$\kappa_s = \frac{3}{r_0^3} \int_0^{r_0} \left\{ \frac{\Delta p}{\Delta p_0} \left(-\frac{1}{v} \frac{\Delta v}{\Delta p} \right) \right\} r^2 dr = \frac{3}{r_0^3} \int_0^{r_0} \left\{ 1 + \frac{\partial p(r)}{\partial r} \frac{\Delta r}{\Delta p_0} \right\} \kappa(r) r^2 dr.$$

An upper limit for the second term of the integrand may be obtained by the following consideration: Let $\bar{\kappa}(r)$ be the compressibility of that part of the liquid which is inside a sphere of radius r around the ion. Then $\bar{\kappa}(r) < \bar{\kappa}(r)$

⁹ Critical Tables III, 54 (1928).

And

$$\left| \frac{\Delta r}{\Delta p_0} \right| = \left| \frac{-r\bar{\kappa}(r)/3}{1+(r/3)(\partial p(r)/\partial r)\kappa(r)} \right| < \left| \frac{-r\kappa(r)/3}{1+(r/3)(\partial p(r)/\partial r)\kappa(r)} \right|.$$

By evaluating this upper limit it is seen that the second term of the integrand must be small, and that a sufficiently close approximation is obtained by using the upper limit multiplied by a correction factor κ_s/r_0 , where a first approximation value of κ_s is used.

For $\partial p(r)/\partial r$ we can write, to the same order of approximation,

$$\partial p(r)/\partial r = -4p(r)/r.$$

Finally, in order to carry out the graphical integration it is more convenient to write:

$$\kappa_0 - \kappa_s = \frac{3}{r_0^3} \int_0^{r_0} \left\{ \kappa_0 - \left[1 + \frac{\partial p(r)}{\partial r} \frac{\Delta r}{\Delta p_0} \right] \kappa(r) \right\} r^2 dr. \quad (11)$$

The values of $\kappa(r)$ are taken from Bridgman's curve, reproduced in Fig. 3.

The result of such integrations for various concentrations is plotted in Fig. 4. In the same figure we have plotted some experimental data due

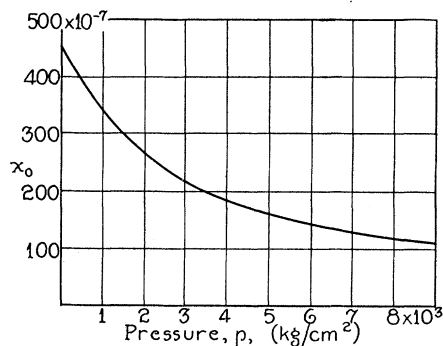


Fig. 3. Compressibility of water at 20°C (Bridgman, 1914).

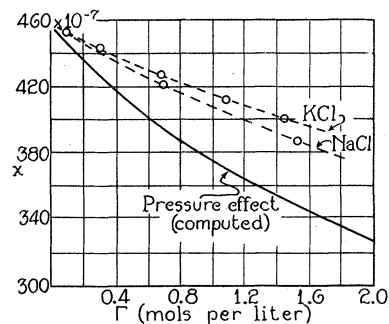


Fig. 4. Compressibilities of aqueous solutions at 20°C.

to Roentgen and Schneider.¹⁰ It will be seen that the experimental compressibilities are higher than those computed from the pressure effect alone. Some pertinent evidence that this may be due to hydration is given in Fig. 5. The data from which this family of curves was plotted also were taken from Roentgen and Schneider¹¹ and show, within the limits of experimental accuracy, that there is a linear relation between the difference in compressibility of any two binary solutions and concentration. In other words, the difference in compressibility is due to an effect which increases linearly with

¹⁰ W. C. Roentgen and J. Schneider, Wied. Ann. **34**, 531 (1888).

¹¹ W. C. Roentgen and J. Schneider, Wied. Ann. **29**, 165 (1886).

the number of ions of the same kind in solution. We know that as long as the supply of water molecules is sufficient each ion of the same kind will produce, qualitatively and quantitatively, the same chemical effect on the water molecules. Therefore whatever the influence of this chemical effect on the thermal properties of the solution, we should expect a linear increase in the effect with concentration.

This linear dependency has previously been pointed out also for a caloric property of electrolytes, namely the specific heat.¹

If, in Fig. 4, one takes the difference between the experimental curve for KCl and the theoretical curve, one obtains a linear relation up to a

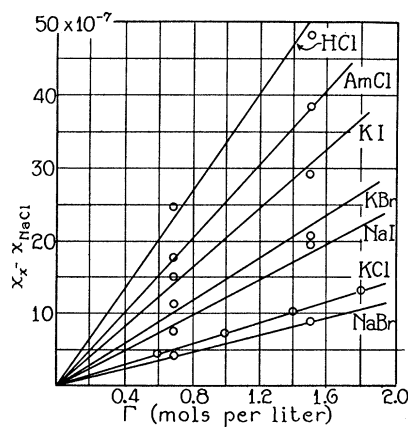


Fig. 5. Showing the linear relation between the difference in compressibility of any two binary solutions and concentration.

concentration of about 0.15 mols per liter. Beyond this point then, our approximation theory yields results which have only a qualitative, but definitely no quantitative significance. The reason for this probably is to be looked for in our method of obtaining the pressure distribution as well as in secondary hydration effects.

From this and previous work¹ we can draw the conclusion that the difference in thermal and caloric properties of dilute solutions against those of the pure solvent is due to the superposition of two effects: First, a physical effect of the ion on the solvent which is predominantly manifested as an internal pressure varying from point to point in the solution. Secondly, a chemical effect of the ion on the solvent, which for dilute solutions increases linearly with the molal concentration.

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